Application of Trace Organic Analysis to Fisheries Environmental Research

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APPLICATION OF TRACE ORGANIC ANALYSIS TO FISHERIES ENVIRONMENTAL RESEARCH

by

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CONTENTS

Abstract/Résumé iv
Introduction 1
Hazard Assessment 1
Field Studies 2
Monitoring Program - Rationale and Organization 2
    Objective 2
    Sampling location and frequency 2
    Chemical analysis 3
    Data evaluation 3
Sampling 3
Environmental Specimen Bank 3
Sample Preparation and Storage for Chemical Analysis 4
Solvent Extraction 4
Sample Preconcentration 4
Sample Cleanup 5
Instrumental Separation and Identification 6
    Gas chromatography 6
    Liquid chromatography 6
    Hyphenated methods 6
Common Aquatic Organic Contaminants 7
Chemical Analysis: Selected Examples 7
    Chlorinated hydrocarbons. 7
        Solvent extraction 8
        Cleanup 8
        Fractionation or group separation 8
        Chromatographic determination 9
    Polycyclic aromatic hydrocarbons 10
        Solvent extraction 10
        Cleanup and fractionation 10
        Identification and quantitation 10
    Chlorinated ethers 11
Precison, Accuracy and Quality Assurance of Chemical Data 11
Conclusions 11
Acknowledgments 11
References 11

ABSTRACT

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Recent literature on chemical analyses of trace organic substances in fisheries environmental research has been reviewed and the need to address the various problems encountered in analyses of a multitude of organic contaminants in the aquatic environment have been highlighted with specific examples.

Organic chemical contaminants enter the aquatic ecosystem in various ways, such as, accidental spill, point-source discharge, urban and agricultural runoffs, municipal waste discharge, ocean dumping operations, and long-range aerial transport. These contaminants are generally found in the aquatic environment only in trace amounts but may be hazardous to the biota. Hazard assessment of the contaminants requires an estimate of their environmental concentrations and whether the chemicals are likely to be persistent and accumulative. The information can be obtained from quality laboratory data. The chemical data are also necessary for trend monitoring and determination of hot spots.

The chemical methods for analyses of trace organics in environmental samples consist of only four steps: solvent extraction, removal of interfering substances, separation into groups and determination of individual components of interest. But even for ubiquitous contaminants like PCB's the steps are not standardized, since no single procedure is sufficient for the wide variety of matrices in which they are found. Analytical methods applicable to PCB analyses are almost as varied as the number of laboratories doing this type of work. The situation is very similar for most other contaminants encountered in fisheries environmental research. The introduction of new chemicals is only increasing the complexity of the problem. Attention is also drawn to deficiencies in sampling design and storage, the need for quality assurance - quality control, and use of reference materials in the analytical laboratory to ensure the quality of data.

RÉSUMÉ

Ray, S. 1987. Application of trace organic analysis to fisheries environmental research. Can. MS Rep. Fish. Aquat. Sci. 1942: iv + 18 p.

On a révisé la documentation récente portant sur les analyses chimiques de traces de substances organiques trouvées au cours de recherches menées en milieu halieutique et, à l'aide de certains exemples précis, on a souligné le besoin de régler les divers problèmes liés aux analyses d'une multitude de contaminants organiques dans le milieu aquatique.

Les contaminants chimiques organiques s'infiltrent dans l'écosystème aquatique de plusieurs façons, notamment par les déversements accidentels, les déversements localisés, les eaux de ruissellement urbaines et agricoles, les déversements de déchets municipaux, l'immersion de déchets en mer et le transport aérien de polluants sur de grandes distances. En général, le milieu aquatique ne contient que des traces de ces matières contaminantes mais elles mettent quand même le biotope en danger. Pour évaluer les dangers que posent les contaminants, il faut estimer leurs concentrations dans l'environnement et déterminer s'ils sont susceptibles de s'accumuler et de persister.

L'information requise peut être tirée de données fiables de laboratoire. Les données chimiques sont aussi nécessaires à l'évaluation des tendances et à la détermination de points chauds.

Il n'y a que quatre étapes dans l'analyse chimique de traces de substances organiques dans des échantillons du milieu: l'extraction par solvant, l'enlèvement de substances parasites, et l'identification et la répartition en groupes de tous les composants qui nous intéressent. Mais même pour des contaminants omniprésents comme le BPC, les étapes ne sont pas normalisées puisqu'il n'existe pas une seule procédure qui soit suffisante pour les innombrables matrices dans lesquelles on les retrouve. Les méthodes utilisées pour analyser le BPC sont presque aussi nombreuses que les laboratoires qui font ce genre d'analyse. La situation est presque la même pour la plupart des autres contaminants découverts au cours de la recherche en milieu halieutique. De plus, la découverte de nouveaux produits chimiques ne fait que compliquer encore le problème. Le présent rapport fait aussi état des lacunes relevées dans les plans d'échantillonnage et l'entreposage des échantillons, et étudie la nécessité de contrôler et d'assurer la qualité et de consulter les ouvrages de référence dans les laboratoires d'analyse afin de veiller à la pertinence des données.

INTRODUCTION

There were 7,454,721 substances and nearly 11.4 million names listed in the Chemical Abstracts at the end of 1985 (ACS 1986). However, the number of synthetic chemicals in use is only about 70,000. Many of these chemicals enter water bodies from a number of sources: urban and agricultural runoff, point source discharge of industrial wastes and accidental spills, municipal waste discharge, ocean dumping operations, and long-range atmospheric transport of pollutants.

Contamination of aquatic ecosystems by point source discharge of pollutants or from diffuse pollution caused by land use has been extensively documented and dealt with in the past. However, contamination of water bodies by pollutants through long-range transport has assumed tremendous significance only recently. For example, the aquatic environments in the Arctic (McNeeley and Gummer 1984; Oehme and Manø 1984; Addison et al. 1986; Hoff and Chan 1986), Antarctic (Peterle 1969; Peel 1975; Tanabe et al. 1983; Kawano et al. 1986) and several other places (Bidelman and Olney 1974, 1975; Murphy and Rzeszutko 1977; Eisenreich et al. 1979; Atlas and Giam 1981; Murphy et al. 1981; Bidelman and Leonard 1982; Weber 1983; Karasek and Hutzinger 1986; Knap et al. 1986) far from any known source of anthropogenic input, have been found to contain polychlorobiphenyls and other organochlorine compounds.

Many of these pollutants in the aquatic system are subjected to chemical and biological transformation in the environment, but very little is known about the toxicity of most of these chemicals or their transformation products to aquatic organisms. Determination of these organic chemicals which occur only in trace amounts in the aquatic environment is fundamental to the solution of fisheries habitat protection problems. A large number of organic chemical contaminants has been detected in commercial products at part per million (ppm) level or less.

This review attempts to focus on problems encountered in analyses of trace organic substances that are normally encountered in a variety of matrices found in aquatic environmental samples and is not an exhaustive survey of literature. Specific examples from recent literature are discussed to illustrate the complexity of the analytical problems that may have to be faced in organic trace analysis. Because of the enormity of the subject, it is possible to consider only a limited amount of the total volume of the published work. Emphasis has been put on organochlorine compounds, since they are ubiquitous and most persistent in the aquatic environment.

HAZARD ASSESSMENT

There are two facets of aquatic contaminants research: reactive and anticipatory. Reactive research responds to issues on a crisis basis. Anticipatory research identifies the contaminants and location of future concern. As part of the anticipatory programs, hazard assessment schemes must be developed to assess potential adverse effects of chemicals already in use and new chemicals proposed for use in the area of concern.

Fisheries environmental problems are generally concerned with limits for safe and aesthetic concentrations of chemicals in water to protect aquatic and marine organisms and with what happens to the chemicals that enter the aquatic environment: evaporation, degradation, bioconcentration or particulate adsorption. The knowledge is used for predictive assessment for industrial and regulatory purposes.

As part of the hazard assessment of contaminants in the aquatic environment, an estimate is required of the environmental concentration of the contaminant, duration of exposure of an organism to the contaminant and the subsequent biological transformation of the contaminant. In essence, the impact-hazard assessment must rely on predicting the fate of the contaminant, that is, the time varying concentrations within the ecosystem compartment of interest.

Except in case of occasional accidents, most contaminants occur in the aquatic environment in only trace concentrations, i.e. part per million (ppm) level or even part per billion (ppb) level. The fate of these chemicals in the aquatic environment can often be predicted from laboratory studies. Physico-chemical properties of the chemicals can be used to predict compartmental distribution of the substance of interest in the environment, and most important from the fisheries aspect, whether the chemical is likely to be persistent and accumulative (Cairns et al. 1978; Pavlou and Dexter 1979; Kenaga and Goring 1980; Veith et al. 1980; van Gestel et al. 1985; Esser 1986). The possibility of environmental or biological breakdown products may have significant implications, since the degradation products can themselves be potentially hazardous. Several typical properties of a chemical that can be used to make predictions of environmental concentrations are listed below:

Property:	Molecular structure
	Solubility
	Water
	Lipid
	Vapor pressure
	Dissociation constant
Rate constants:	Photodegradation
	Biological degradation
	Chemical degradation
	Evaporation or volatilization
	Sediment or particulate binding
	Uptake by organisms
	Depuration by organisms
Partition coefficients:	Octanol-water
	Air-water
	Sediment-water

Predictions regarding concentrations and the fate of any chemical from the data gathered in the laboratory will require field confirmation with sensitive analytical procedures for the chemical and for any of its significant degradation products. The lack of definitive analytical procedures that can be applied to determine the contaminants in the variety of matrices that are normally encountered in fisheries environmental research is often a serious handicap. Appropriate analytical methods have to be developed before specific problems can be handled. The required sensitivity and specificity of the analytical procedures become greater as the

evaluation procedures become more and more sophisticated. Consequently, the cost and effort expended in any analytical method development and in its application are geared to the needs of hazard evaluation.

FIELD STUDIES

There is a need to integrate laboratory and field studies and to establish a relationship between adverse effects of exposure of any chemical to aquatic animals in the laboratory study with the effects observed in the field. Though neither laboratory nor field studies alone can solve all problems in contamination research, very few field studies have been undertaken to confirm laboratory observation (Schnoor 1982; Adams et al. 1983; Chapman 1983; Lee and Jones 1983; Suter et al. 1985).

Field studies suffer from uncontrollable baseline variability. The biological populations may undergo diurnal, seasonal or annual fluctuations of one or more orders of magnitude. Superimposed on this is a smaller degree of variability due to man-induced effects, including those of toxic chemicals. However, confirmative field studies can be designed to answer critical questions of environmental safety. These studies should be supplemented by monitoring for ultimate confirmation of safety under use conditions.

MONITORING PROGRAM - RATIONALE AND ORGANIZATION

Environmental monitoring is a part of the assessment of chemical hazards to fisheries. It is required to provide general background information about fisheries habitat, to evaluate the effectiveness of existing pollution control measures and to determine time trends of pollutants in the aquatic environment. In general, it is vital for continued protection of fishery resources.

Monitoring the health of the aquatic environment to assess the current status of the system is extremely important. The concentrations of polluants in species of existing and potential commercial value may reflect the ambient levels in the aquatic environment. A priority, for fisheries management, should be the major fishing areas with particular concern for industrialized estuaries and coastal areas known to be receiving waters from industrial and municipal point sources of contamination.

Open water dump sites for industrial wastes, harbor dredgings and sewage sludge should warrant special attention. However, if the estuaries and the coastal areas do not have persistent pollutants and support abundant and self-reproducing native fish and shellfish communities, then it is expected that the environments of the deeper waters will also be biologically favorable for the biota.

For a monitoring scheme to be effective, it must clearly define the species to be examined, size of sample, biological size range, age, sex, season of the year, sample storage methods, analytical techniques and use standard reference materials in chemical analysis. In any comprehensive monitoring program, sampling and analyses of the sediment and water column are integral parts of the scheme.

Structurally, the ecosystem monitoring programs should have four components:

1. Delineation of objectives (baseline determination, hot spot or trend monitoring)
2. Determination of sampling location and frequency
3. Chemical analysis of environmental samples
4. Synthesis and evaluation of chemical data.

OBJECTIVES

The importance of identifying the purpose of environmental monitoring before undertaking sampling and chemical analysis cannot be overemphasized. The effective strategy adopted will, in general, vary with whether the sampling is for: a) regulatory or legal purposes, b) time-trend analysis or c) hazard assessment.

SAMPLING LOCATION AND FREQUENCY

The sampling scheme may involve:

Benthic sampling
"Mussel watch" type sampling
Water quality sampling

The benthic component should measure toxic chemicals in surface sediments and bottom dwelling organisms taken from the same area. This component of the program is of prime importance in the Canadian Maritimes since the bottom dwelling organisms constitute more than 80% of the landed value of the fishery in this region.

The "mussel watch" type component refers to mussels or other suitable bivalves to be analyzed for polychlorinated biphenyls (PCB's), other chlorinated hydrocarbons, polyaromatic hydrocarbons (PAH) and lipid contents. The utility of "mussel watch" type sampling for monitoring of coastal pollution has been amply demonstrated (Goldberg et al. 1978; Farrington et al. 1983; Goldberg 1986). The sediments collected from the same area should also be analyzed for the same group of chemicals. The determination of regional trends in sediment quality is necessary to identify and delineate those areas that are excessively contaminated with toxic chemicals and therefore most in need of remedial actions. Sediment deposition zones accumulate and integrate the chemical inputs over time. Chemical data from analysis of sediment samples from these zones can be helpful in determining the history of accumulation of inputs and geographic trends in degrees of contamination.

The term "water quality" almost always implies some value judgments and refers to the suitability of water for its desired uses. The consensus is that "water quality" should be taken to mean the physical/chemical/biological characteristics of water necessary to sustain a desired use which is, in the present case, a viable and self-sustaining fishery. Productive populations of fish can only exist in waters where all habitat characteristics, including physical and chemical factors, are within limited ranges. The necessity for the protection of

aquatic life from the adverse effects of a variety of chemicals in use has gained wide acceptance in recent years. The required water quality criteria levels for a number of chemicals were defined by National Academy of Sciences and National Academy of Engineering (1972) and later updated by the U.S. Environmental Protection Agency (EPA 1976). However, a large number of chemicals in current use are still not covered and the gap is gradually increasing with the introduction of new chemicals.

The water quality component is normally the weakest link in any toxic chemicals monitoring program because of the cost involved in detecting and identifying the sub-part per trillion (ppt) level of toxicants in the water column. Such efforts should be undertaken only when the perceived hazard requires or cost permits. Other physico-chemical factors like temperature, salinity or oxygen levels should be measured on a regular basis since these measurements may be crucial in estuarine or near-coastal situations, where they may affect the relevant rate constants of environmental transformation of the chemicals.

CHEMICAL ANALYSIS

A complete scheme of trace organic analysis of fisheries environmental samples generally consists of sampling, extraction, preconcentration, prefractionation and analysis using either gas chromatography, liquid chromatography or a combination of chromatographic-spectrometric methods. Quite often some of the steps overlap or are combined to facilitate analysis. The processes are described below.

DATA EVALUATION

The synthesis and evaluation of a data base is of crucial importance for regulatory and environmental management and to the environmental scientists for time-trend analysis. The quality control-quality assurance of the data is fundamental for any decisions that are based on the analytical results and is discussed later.

SAMPLING

Sampling is one of the most important steps in chemical analysis, but its planning and execution is often neglected. Normally, the analyst has very little to do with actual sampling. The samples received in the laboratory are considered valid and substantial analytical work may be undertaken on that assumption. The purpose of sampling is to obtain specimens that represent the situation being studied. Furthermore, "the quality and utility of analytical data depend critically on the validity of the sample and the adequacy of sampling program" (ACS 1983). The guidelines for sampling protocols in environmental analysis have been proposed by the Committee on Environmental Improvement of the American Chemical Society (1980, 1983) and, for fisheries research in particular, by FAO (1976, 1983) and I.O.C. (1984). However, most of the protocols that have been defined are limited only to organochlorines in aquatic environmental samples, i.e. water, sediment and biota. Several salient features of sampling for fisheries environmental research are discussed below.

Basically, there are three kinds of sampling programs that may be used in fisheries environmental research. Intuitive samples are those that are collected on the basis of general knowledge, past experience and a lot of guesswork. Statistical sampling is based on a plan that can provide probabilistic conclusions. Protocol samples are those that are required for regulatory purposes. The sample size, frequency of sampling, etc. are often specified.

Proper specimen sampling is particularly important where the trace contaminant data are used for regulation and management of fishery resources. Sampling and devising of proper sampling plans are often complex and should invariably be developed with statistical input. This is seldom done in practice and the environmental chemistry literature is replete with examples of haphazard sampling undertaken for monitoring programs.

Because the aquatic environment is typically heterogenous, a large number of samples must be analyzed to obtain meaningful data representative of a compartment. Quite often, in order to reduce the labor and cost involved in analyzing individual samples, a large number of samples are combined to provide a homogenous composite sample for subsample analysis. However, this procedure can only provide an average compositional value. If composition profiles or the variability of sample population is of interest, then many samples have to be collected and analyzed individually.

A statistical approach to define the number of samples to be taken is possible when the distribution and standard deviation of the population are known or can be assumed. Similarly, the number of replicate measurements required on a sample, composite or individual, to achieve a mean value with a given confidence interval can also be statistically determined.

Theoretical principles involved for proper sampling protocol in environmental analysis have been discussed in detail (Kratochvil and Taylor 1981; ACS 1983; Kratochvil 1985).

ENVIRONMENTAL SPECIMEN BANK

The concept of an environmental specimen bank for archiving biological and other environmental samples for retrospective analysis has in recent years emerged as an essential component of systematic environmental monitoring and, in particular, trend analysis (Wise and Zeisler 1984). Sample banking involves preservation of samples under unequivocal conditions that ensure their integrity over an extended period of time. It is an expensive program and hence must be restricted to selective samples which are of unquestionable integrity.

There are several reasons for establishing a specimen bank, especially for fisheries environmental research. First and foremost, it is physically impossible to monitor all fishery resources for all hazardous contaminants that enter the aquatic ecosystem. Thus, a program can only focus on the measurement of specific chemical species that have already been proved to be hazardous to fishery resources and only in areas

that are considered to be of interest. Secondly, screening for large numbers of organic compound classes is difficult because of the requirements of selective extraction, digestion, isolation procedures and detection of various compound classes. The multitude and diversity of environmental organic pollutants and the analytical requirements necessary to even attempt to monitor all these pollutants serve as justification for the need to archive environmental specimens for retrospective analysis. The long-term storage of carefully selected samples would provide an important component of real-time monitoring of the environment as well as an environmental history of the pollutants. It may also be an invaluable help in future evaluation of the distribution of as yet unidentified pollutants. For example, in recent years, retrospective analysis of herring gull eggs collected in the early 1970's and stored in a specimen bank was used to confirm a decrease in 2,3,7,8-TCDD (Elliott 1984). The chemical was not known to be a problem at the time of collection of the samples.

The German Environmental Specimen Bank program is quite comprehensive and includes specimens from freshwater and marine environments (Stoeppler et al. 1982, 1984). In the National Bureau of Standards pilot program in the U.S. (Wise et al. 1984), only one aquatic specimen, Mytilus edulis, is collected. The Canadian Wildlife Service is already opeating an ad hoc storage facility for its various monitoring programs for toxic chemicals in wildlife (Eliott 1984). A similar program should be implemented in fisheries environmental research on a national scale as soon as possible. A start has already been made on a very small scale at the National Water Research Institute in Canada.

SAMPLE PREPARATION AND STORAGE FOR CHEMICAL ANALYSIS

Most environmental samples contain low levels of organic pollutants. Extreme caution must be taken for sample collection, processing and storage. Storage conditions should ensure minimal microbial degradation, photochemical or chemical decomposition and loss of volatile components due to evaporation prior to chemical analysis. This is essential to ensure the data quality. When a sample has been obtained, it often requires one or more pretreatments prior to actual measurement of the contaminants which may introduce bias variance and further contamination to the analytical process. Necessary protective steps to ensure sample integrity for analysis of organochlorines and other organic pollutants in biological samples have been specified by Food and Agriculture Organization of the United Nations (FAO 1976, 1983), U.S. EPA (Harrison et al. 1981) and U.S. NBS (Wise et al. 1984). Similar protocols are available for PCB's in ocean waters (IOC 1984). Sample handling for analyses of polychlorinated terphenyls (PCT's), polychlorinated naphthalenes (PCN's) and other organochlorines are essentially the same as those adopted for PCB's.

SOLVENT EXTRACTION

To analyze for trace organic contaminants in solid, liquid or gaseous environmental samples, it is necessary to selectively extract these compounds from the environmental matrices in which they are found. Proper choice of an extraction solvent and its purity is often critical in the sample preparation procedure (Bowers et al. 1981a). Quite often a solvent that efficiently extracts a compound from a sample matrix may fail to remove the same compound with the same degree of efficiency from another matrix. For example, recovery of TCDD by methanol from incinerator fly ash is poor compared with the higher extraction efficiency of methanol for the same compound from airborne particulate matter (Hill et al. 1977). Quantitative recovery of a spiked sample by a solvent or a solvent mixture does not ensure quantitative recovery of the same contaminant(s) by the same solvent system from a naturally contaminated environmental sample. Bellar et al. (1980) compared PCB extraction efficiency from naturally contaminated and spiked sediment samples by three techniques: a) Soxhlet extraction (90 hexane:10 acetone), b) ultrasonic extraction with acetone and c) steam distillation with hexane and water. All three methods worked equally well with the spiked sample but the Soxhlet extraction had much higher efficiency than the other two with naturally contaminated sediment. The observations were supported by Wegman and Hofstee (1982) who obtained lower recovery from samples 30 d after spiking compared with the samples analyzed 2 d after spiking. They suggested that spiked material after 30 d approximated the real world situation more closely than the freshly spiked sample.

Lee et al. (1986) reported that ultrasonic extraction of di- and tri-chlorobenzenes with hexane-acetone (1:1) yielded only 50-70% of the corresponding values obtained by Soxhlet extraction with the same solvent system. Onuska and Terry (1985) reported that recoveries for di-, tri-, tetra-, penta- and hexachlorobenzenes in spiked sediments ranged from 55±11% for Soxhlet extraction, 48±12% for sonification and centrifugation and 81±12% for steam distillation method. Surprisingly, the ultrasonic method recommended by Environment Canada in 1979 for extraction of PCB's and organochlorine insecticides from sediment samples is still in use for extraction of the organochlorines.

SAMPLE PRECONCENTRATION

In many trace analyses, a preconcentration step is unavoidable prior to quantitative analysis. The classical techniques such as freeze drying, Soxhlet extraction or steam distillation have serious limitations in terms of recovery, capacity and loss of sample during processing. The most commonly used method is solvent reduction performed following extraction by rotary evaporation under reduced pressure. The technique is rapid but the volatile components are largely lost. In a study on recovery of chlorobenzenes from bottom sediments, Lee et al. (1986) reported that of the four methods tried, solvent evaporation using a Snyder column gives the least loss of the components. Severe losses of even the nonvolatiles can be experienced when preconcentration procedures require complete evaporation of the initial solvent. Bowers et al. (1981b) have demonstrated appreciable loss of relatively nonvolatile compounds like chlorinated dioxins, even when the evaporation was carried out under very gentle conditions.

The apparatus that is most often used as an alternative to the rotary evaporator is the Kuderna-Danish concentrator with a Snyder column which has a better recovery (Webb 1975). Further concentration to as little as 0.1 mL is usually done by gas stream-water bath method. High purity air, nitrogen or helium is generally used to avoid introduction of artifacts. Some sample loss may still be experienced through neutralization but may not be critical so long as the composition of the organics on the glass surface remains the same as the composition in the solution. The largest and most irreproducible losses generally occur at volumes less than 0.5 mL. Reduction below this level should be avoided if at all possible.

Preconcentration with sorbent traps are recently being widely used. The technique, if applied to water samples, combines the sampling and preconcentration steps and reduces sample handling. The use of microreticular XAD resins packed into glass tubes for sampling of large quantities of water gives 90-100% recoveries of compounds such as pesticides, alkyl benzenes, organohalogens, polyaromatic hydrocarbons, phenols, etc. (Junk et al. 1974; Dressler 1979; Rees and Au 1979). In the past few years, the use of liquid chromatographic packing materials for trace enrichment, either on column or on-line with precolumn, has also become a powerful tool in trace analytical work. The precolumn concept has many potential areas of application. Many interfering substances can be eliminated by choosing more selective materials such as polar chemical bonded phases, ion exchangers and metal loaded surfaces. Such precolumns can often be used in a series to isolate different fractions or groups of compounds for final determination.

No single preconcentration procedure is sufficient for the wide variety of applications for trace organic analysis. Though the existing methods give acceptable recoveries for most applications, there is still room for improvement. Preconcentration techniques for trace analysis of organic compounds have recently been reviewed by Karasek et al. (1981).

SAMPLE CLEANUP

Though a few samples may be suitable for direct chemical analysis after extraction and preconcentration steps, the majority of environmental samples need extensive cleanup for separating the compounds of interest from animal lipids and other natural organic substances before they can be analyzed. The rule is "a clean sample gives best results."

If an analysis is to be attempted with a detection of only moderate selectivity, a substantial cleanup procedure may have to be undertaken. That is, the concentration of the derived trace component should be enhanced while the concentration of possible interfering substances in the sample matrix is decreased.

Solvent partitioning can be used for this process, particularly if the sample has distinct acidic or basic properties. For example, phenolic compounds can be extracted into water-immiscible organic solvents from aqueous samples. These acidic samples can then be back-extracted into basic aqueous solution, which can then be washed with immiscible organic solvents to remove extraneous materials. Acidification of the basic solution, followed by extraction into a suitable organic solvent and evaporation, may give an enriched clean extract for analysis by a suitable method. The combination of suitable partitioning systems for clean-up of extracts is very large and has been used extensively in the past.

Ion exchange resins can often be used effectively for selective absorption of ionic compounds from certain media. The extraneous materials in the sample are then eluted from the column by appropriate washing steps and the compound of interest can then be desorbed from the column by a change in the mobile phase to produce a cleaned up fraction.

Adsorption methods are quite often used in cleaning environmental samples. For example, PCB's are weakly absorbed in columns of silica gel, florisil, etc. These less polar trace organics are then readily eluted while more polar, tightly held co-extractives are held in the column. Absorbent columns for cleanup operation will tolerate large amounts of co-extractives while still producing effective cleanup. However, the activity of the absorbent must be carefully controlled for reproducible results. Solvent purity also affects the recovery of the compound from the column. Zitko (1971) showed that the elution profile of Aroclor 1254, DDT and DDE recovered from silicic acid column depended on the amount of benzene normally present in hexane used for eluting the column.

Size separation is achieved by either gel permeation, column chromatography or HPLC on sphadex, LH20, LH60 or molecular sieves.

Exclusion or gel chromatography (GPC) is often an effective technique for cleaning up extracts containing trace organic components and is being increasingly used for environmental samples. This technique is based on separation of materials as a function of their molecular size and is useful for separating large molecular weight, interfering substances from trace components of lower relative molecular mass. Typically, gels with small pores, designed to retain only compounds of lower relative mass, are used for initial clean-up. Gel chromatographic separation has the additional advantage that there is an almost complete absence of chemical change during the separation, making this one of the mildest separation techniques.

In recent years, automated sample cleanup with High Performance Liquid Chromatography (HPLC) has also been applied. The two variations adopted are a short precolumn before the analytical column and column switching for "heart cutting" (Deans 1981). Column switching permits several different techniques to be carried out, the most popular of which include sample cleanup, trace enrichment and multicolumn chromatography (column programming). Though these techniques have been widely used for drug and pesticide analysis (Kargar et al. 1983; Ramsteiner 1986), applications in environmental trace organic analysis are still rare.

Specific examples of sample cleanup procedures are dealt with in more detail in the section on chemical analysis of specific classes of compounds.

INSTRUMENTAL SEPARATION AND IDENTIFICATION

In analytical laboratories, chromatography is the predominant separation method, with Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC) used most often for final separation. The methods are complementary. Detection systems vary widely and the data reduction are performed by dedicated integrators or by computer-based data systems. The most recent addition to the list of separation techniques is the capillary super critical fluid chromatography (SFC) (Chester 1986) but, as yet, the applications are very limited. Typically, the detectors for SFC are modified GC or HPLC detectors. The common detectors in GC, HPLC or SFC provide mostly quantitative rather than qualitative information. Spectrometric detectors coupled with chromatographic systems are the only means to obtain unambiguous qualitative information. The most successful and widely used system is the coupling of GC with the mass spectrometer (GC-MS) as a detector. Recent instrumental developments and the application of MS as a compound-specific detector for chromatographic analyses have been reviewed by Grayson (1986). Gas chromatographs, coupled with Fourier transform infrared spectrometry (GC-FTIR), are also being applied extensively (Griffiths et al. 1983).

GAS CHROMATOGRAPHY

Gas chromatography is still the method of choice for separation and identification of most volatile and non-labile compounds. A variety of specific and non-specific detectors are available for GC. Even the nonvolatiles can be chromatographed after formation of suitable detector-oriented chemical derivatives which may render them volatile. These derivatized compounds can be quantitatively identified at trace levels in complex mixtures against the organic background matrix using a minimum cleanup procedure. GC methods for a large number of environmental contaminants have been standardized and are being routinely applied for determination of various contaminants in fisheries environmental research with varying success.

Currently, the halogenated aromatic hydrocarbons such as polychlorinated biphenyls, chlorinated benzenes, and chlorinated pesticides are routinely analyzed by GC with an electron capture detector. The method is extremely sensitive but cannot unequivocally identify any compound unless used in conjunction with a spectrometric method. A large number of other compounds can be analyzed by GC with a variety of versatile and specific detectors without going through derivatization procedures. Very specific problems like isomer specific separation and quantification have become much easier with the introduction of capillary columns. Isomer specific analytical schemes have been designed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Choudhary et al. 1983; Buser and Rappe 1984; Rappe 1984). Similar schemes have been published for PCB's (Pellizzari et al. 1985) and polychlorinated naphthalenes (Jansson et al. 1984).

Since the 1970's, the PCB's in environmental samples have been almost exclusively analyzed on packed columns and the results expressed in terms of technical formulation equivalents such as Aroclor 1254 and 1260. In recent years, with the availability of capillary columns, the trend is to analyze the mixture in terms of individual components for more comprehensive information. However, problems have arisen in comparing results from capillary columns with previous studies involving packed columns. Duinker et al. (1983) have reported that capillary column results for PCB's were 30-70% below values for packed columns while values for α-HCH, Y-HCH, dieldrine and p,p'-DDD were higher. HCB levels were 60-90% lower. Musial and Uthe (1983) have also reported obtaining lower values for PCB's in herring oil analyzed by capillary column than by packed column.

LIQUID CHROMATOGRAPHY

Modern liquid chromatography (LC) has several advantages over gas chromatography. Liquid chromatography has a much wider range of applicability and is preferred for analysis of materials that are nonvolatile, have low volatility, are labile or are ionic. Compounds are rarely degraded by LC and usually it is not necessary to prepare stable, volatile derivatives as is often required for GC analysis. Two chromatographic phases are available in LC for selective interaction with sample components as compared with only one in GC. In addition, a greater variety of separation methods exist in LC (i.e. liquid-liquid, liquid-solid, ion exchange, exclusion). Moreover, chromatographic separation in LC is favored by the use of lower temperatures which allow effective intermolecular interactions. These combinations offer a wider variety of selective interactions and a greater possibility of achieving the high resolving power needed for trace analysis in a complex mixture. One of the shortcomings of LC is often inadequate sensitivity and selectivity in the detection process. This can be overcome by trace enrichment and consequent sample cleanup with precolumn (Frei and Brinkman 1981) or by chemical derivatization (Frei and Lawrence 1981, 1982). A large variety of detectors is available for liquid chromatograpy (Yeung and Synovec 1986) but the most common HPLC detectors are UV-VIS absorbance, fluorescence and electrochemical detectors. The range and applicability of derivatization in determining various classes of compounds (Frei and Lawrence 1981, 1982) as well as the pros and cons of derivatizing before and after separation by HPLC (Frei 1979) have been reviewed.

High performance liquid chromatography has been extensively applied for analyses of various pesticides (Frei 1981; Lawrence 1982; De Kok et al. 1984), PAH (Bartle et al. 1981; Lawrence and Das 1986) and nonvolatile organics in river water (Crathorne et al. 1984). Currently, HPLC is the recommended method for analyzing PAH (Fed. Regis. 1979). Applications to fisheries environmental problems are practically nonexistent but the technique offers a tremendous scope for research and application.

HYPHENATED METHODS

Identification of unknown compounds based on only chromatographic retention times is not unequivocal. Some of these uncertainties have been resolved by application of other techniques in conjunction with comparison of retention times, e.g. MS (Duinker and Hillebrand 1983; Parker et al. 1983; Buser and Rappe 1984; Rappe 1984; Pellizzari

et al. 1985), infrared and nuclear magnetic resonance (Mazzola et al. 1984).

The single most important factor contributing to our ability to identify specific trace organic compounds in environmental samples has been the development of combined GC-MS. Significant advances also have been made on interfacing high performance liquid chromatographs with MS and applying this technique in solving pesticide problems (Levsen et al. 1983; White et al. 1983; Bottomley and Baker 1984; Voyksner et al. 1984).

Negative-ion chemical ionization (NCI) mass spectrometry used as a detector for capillary GC is uniquely suited to measuring trace polyhalogenated organics in environmental samples because of its high sensitivity for these compounds and its virtual transparency to other potentially interfering molecules (Kuehl et al. 1980; Dougherty 1981). Furthermore, it provides molecular ion information, a very desirable feature, when examining complex environmental and biological samples. The technique has been widely used in analysis of PCB and other organohalogens (Crow et al. 1981; Rappe 1984; Pellizzari et al. 1985). During the past few years, pulsed positive ion negative ion chemical ionization (PPINICI) has been available, allowing rapid switching between positive and negative chemical ionization for acquiring simultaneous information (Hunt et al. 1976). The technique has been successfully used for the past few years to identify several contaminants in the aquatic environment (Zitko 1983; Garnett 1985; Zitko et al. 1985) and offers excellent opportunities for further application in fisheries environmental research.

COMMON AQUATIC ORGANIC CONTAMINANTS

Analysis at part per billion (ppb) and sub-nanogram levels have become routinely common in environmental research in the past few years. The activity in the field is reflected by the large number of reviews, books and symposium proceedings published in recent years on such subjects as analysis of PCB's (Afghan and MacKay 1980; Musial and Uthe 1983; Onuska et al. 1983; Pellizzari et al. 1985; Erickson 1986), chlorinated dioxins (NRCC 1981; Hutzinger et al. 1982; Karasek and Onuska 1982; Choudhary et al. 1983; Rappe 1984; Keith et al. 1985; Hutzinger et al. 1986), polyaromatic hydrocarbons (Jones and Leber 1979; Neff 1979; Bartle et al. 1981; Lee et al. 1981; Bjørseth 1983; Cooke and Dennis 1983), pesticides (Das 1981; Chau and Afghan 1982; FDA 1982), and pyrethroids (Miyamoto et al. 1981; Zweig and Sherma 1984), to name only a few. Health and legal decisions are being made on the basis of these results but controversies abound about the use and absolute validity of many analyses done at this level. This has led to considerable interest in trace analysis and the development of new and, hopefully, more reliable methods. However, trace analysis for organic contaminants in fishery resources is still a largely neglected field in areas other than organohalogen compounds, oils and a few pesticides. The need for method development for identification and quantification of trace organic contaminants in water (particularly marine), sediment and aquatic biota cannot be overemphasized. Proper clean-up of environmental samples is expected to leave only the compounds of interest in a suitable solvent for chemical analysis. Infrared, ultraviolet and fluorescence spectra at this stage may be of some help in determining the compound class.

The prefractionation may still be necessary as in the case of analysis of PCB's where they are separated from other organochlorines like DDT, toxaphene, lindane, dieldrin and heptachlorepoxide before analysis by packed column gas chromatography. The separation step is absolutely crucial, otherwise unusually high values are quite likely. For example, DDT values reported prior to 1966 are, now, believed to be high because of cross-contaminating peaks from PCB's. The chlorinated biphenyls were identified to be an environmental contaminant at that time and separation techniques were developed to determine the two groups separately without cross contamination. Similar problems have also been encountered with toxaphene. However, this separation step may not be necessary, if the analysis is done by capillary columns, using MS detector.

The contaminants that are of fisheries environmental concern in the Maritimes are primarily:

- Chlorinated hydrocarbons
  - Insecticides, e.g. HCB, DDT group, toxaphene, chlordane, etc.
  - Industrial chemicals, e.g. PCB's, PCT's, PCQ's, PCDD's, PCDF's, chlorinated benzenes, naphthalenes, etc.
- Phenols and chlorinated phenols
- Polycyclic aromatic hydrocarbons (PAH)
- Other pesticides, e.g. organophosphates, carbamates, etc., and forest spray products, e.g. pyrethroids
- Kraft mill effluents
- Others, e.g.
  - Detergents
  - Nitrosamines
  - Azaheterocyclics
  - PCB replacement compounds, e.g.
    - Diphenyl ethers
    - Polychlorinated ethers
  - Industrial chemicals, etc.

CHEMICAL ANALYSIS: SELECTED EXAMPLES

CHLORINATED HYDROCARBONS

Chlorinated hydrocarbons of environmental interest are all man made. Two groups are of concern: a) pesticides and their metabolic products and b) industrial chemicals like polychlorobiphenyls (PCB's). The primary source of chlorinated pesticides in the environment is the extensive agricultural and forestry applications. Though their use has long been discontinued in Canada, they are ubiquitous in the aquatic environment.

PCB's are chlorinated derivatives of biphenyl, with 209 possible isomers. Similar analogous series of polychloroterphenyls (PCT's) and polychloroquarterphenyls (PCQ's) are also of concern. Recently, another group of chemicals, polychlorodibenzodioxins (PCDD's) and polychlorodibenzofurans

(PCDF's) have been found in fishery products (Niemann et al. 1983; O'Keefe et al. 1983; Ryan et al. 1983; Stalling et al. 1983), and have caused serious concern because of their extremely high toxicity. The PCDD's and PCDF's have 75 and 135 positional isomers, respectively.

Although the halogenated hydrocarbons are ubiquitous in the environment and are major contaminants in the aquatic ecosystem, there is still no consensus on a standard method for analysis for the chlorinated hydrocarbons. A recent literature survey indicates that the quest for a better chromatographic method for simultaneous separation and quantitation of the PCB's, PCDD's and other organochlorines still continues.

Any efficient extraction method employed to extract chlorinated hydrocarbons also yields considerable amounts of undesirable coextractives like lipids, which have to be removed before the chlorinated hydrocarbons can be separated into individual components for identification and quantification by gas chromatography. Four sequential steps are involved before a sample can be chromatographed:

1. Solvent extraction - involves extraction of the contaminants from a variety of aquatic environmental samples. Unfortunately, lipids and other natural biogenic substances are also coextracted.

2. Clean up - separation of lipids, waxes or other polar extractives

3. Fractionation of organochlorines (OC's) into various groups to simplify chemical analysis. Removal of sulphur from sediment extracts (not necessary for water or biota). Subsequent concentration of the respective fractions for chemical analysis.

4. Chromatographic determination.

Solvent extraction

Various methods have commonly been employed for extraction of organochlorines from aquatic environmental samples. The more common ones are listed below:

i) Extraction of homogenized samples with a polar solvent such as acetonitrile (Environment Canada 1979).

ii) Blending with anhydrous sodium sulphate and subsequent cold extraction with ether followed by acetonitrile (EPA 1980) or acetone (Galloway et al. 1983).

iii) Blending the sample with anhydrous sodium sulphate followed by Soxhlet extraction with hexane (Zitko et al. 1974) or 59+41 hexane-acetone (Veith et al. 1975).

iv) Extraction of sample using 35:10 acetone-hexane followed by 9:1 mixture of hexane-diethyl ether (FAO 1983).

v) Exhaustive steam distillation and solvent extraction in hexane of homogenized sample in a modified Nielsen-Kryger steam-distillation apparatus (Veith and Kiwus 1977).

To the best of my knowledge, relative efficiency of extraction of organochlorines from aquatic environmental samples by different methods has yet to be studied.

Cleanup

The cleanup steps normally employed for OC's are summarized below:

Liquid-liquid partitioning involves partitioning the extract which can be in either a polar or a non-polar solvent with an immiscible solvent of opposite polarity. The polar extractives which dissolve in the polar solvent are then discarded. Normally, hexane is the non-polar phase and water or water/acetonitrile is the polar phase (Chau and Babjak 1979; Environment Canada 1979; Oliver and Bothen 1982). Sometimes sodium chloride is used to "salt out" the organochlorines from the polar phase for efficient recovery into the non-polar phase (Environment Canada 1979; Plumb 1981).

Fractionation or group separation

This is achieved by adsorbtion chromatography (column, thin-layer or high performance liquid chromatography on silica, alumina or florisil). Adsorption chromatography is also the most widely used cleanup method of organochlorine sample extracts. The technique has the distinct advantage in that not only are the OC's separated from the lipids, but a preliminary fractionation of the OC's is also effected, if gradient elution is applied to elute the OC's. Though florisil is the most commonly employed adsorbent, silica and alumina have also been successfully employed. The OC's are eluted from florisil by petroleum ether followed successively by i) petroleum ether + 6% diethyl ether, ii) petroleum ether + 15% diethyl ether and, finally, iii) petroleum ether + 50% diethyl ether. The first eluate fraction contains PCB's, DDE, BHC, aldrin and heptachlor; the second contains DDT, DDD, lindane, chlordane, methoxyclor and heptachlor epoxide; the third contains endrin, dieldrin and α-endosulfan and the fourth contains β-endosulfan.

Deactivated alumina has been used for clean-up of extracts, but the technique is not very efficient and a further cleanup step is normally required to separate the OC's into groups that can be analyzed by gas chromatography (Ernst et al. 1976; Wegman and Hofstee 1982). The advantage of using alumina column is that it has a high capacity for the lipids and the column material can be prepared to give reproducible results.

Silica gel is superior to alumina because of its selectivity and capacity to fractionate the OC's. PCB's can be separated from most OC's with suitable choice of eluents (Zitko 1971). However, it is not very effective for lipid retention.

Charcoal column (Teichman et al. 1978) and charcoal on polyurethane foam (Huckins et al. 1978; Chau and Babjak 1979; Lee et al. 1982) have been successfully used for the fractionation of extracts.

Gel permeation chromatography (GPC) has also been used to separate high molecular weight lipids (approx. 500-1500 D) from low molecular weight OC's, which are mostly less than 500 D (Stalling et al. 1972; Vieth et al. 1975; Kuehl and Leonard 1978;

EPA 1980; LeBel and Williams 1986; Norstrom et al. 1986). However, GPC is not very effective in fractionating the OC's and has to be followed by one of the adsorption chromatographic methods for group separation before gas chromatography. The strength of the GPC lies in its ability to handle the large amounts of lipids normally found in animal extracts.

Sulphur is normally found in most sediment samples and has to be removed before the extracts can be analyzed by gas chromatography with an electron capture (EC) detector. Several methods are available for sulphur removal by precipitation, but only two are widely used - either by reacting with elemental mercury (Goerlitz and Law 1974) or activated copper powder (Blumer 1957; Plumb 1981). Both PCB's and OC pesticides are stable to treatment by mercury (Chau and Lee 1980; Addison and Nearing 1982) and activated copper powder (Chau and Babjak 1979; Plumb 1981). However, activated copper is normally the method of choice since it gives better recoveries and poses less environmental hazard (Lee et al. 1982).

Concentration of the respective fractions for gas chromatographic analysis can be achieved by sample preconcentration methods described earlier.

Chromatographic determination

The final step is the chromatographic determination of the individual components in the concentrate. Gas chromatography with EC detector is still the method of choice for analyses of chlorinated hydrocarbons such as PCB's, chlorinated pesticides and other organohalogens. The method is extremely sensitive but cannot unequivocally identify any compound unless used in conjunction with a spectrometric method. Some of the analytical uncertainties have been resolved by comparison of retention times of these components, along with application of techniques like mass spectrometry (Onuska et al. 1980; Duinker and Hillebrand 1983; Parker et al. 1983; Buser and Rappe 1984; Rappe 1984; Pellizzari et al. 1985); infrared spectroscopy (Griffiths et al. 1983; Schneider et al. 1985) and nuclear magnetic resonance (Mazzola et al. 1984). Although use of a MS detector has the analytical advantage over an ordinary EC detector, the equipment is rather expensive and beyond the means of most laboratories involved in environmental research. GC-MS is mainly used for two reasons: first, if an analysis requires highly specific detection owing to the presence of interfering peaks, i.e. if the sample cleanup does not isolate compounds of interest sufficiently well from the remainder of the sample; and second, if the available GC detection techniques (e.g. F.I.D.) do not provide sufficient sensitivity.

Gas chromatographic methods for a large number of environmental contaminants have been standardized and are being routinely applied with varying degrees of success in fisheries environmental research. However, these empirically calibrated methods such as Webb and McCall (1973) are slowly becoming obsolete with the wider availability of high resolution capillary columns. The empirical method is being replaced either by measurement of groups of congeners with the same degree of chlorination or the total of all congeners. Isomer specific separation and quantification schemes have been reported for PCB's (Pellizzari et al. 1985) and polychlorinated naphthalenes (Jansson et al. 1984). Similar schemes have also been published for pollutants like polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Choudhary et al. 1983; Buser and Rappe 1984; Rappe 1984).

The quantification of the PCB's is accomplished by comparing the chromatographic peak heights or areas of the major components in the extract with the peak heights of the same components in the standard. However, the response of electron capture detector is disproportionate, i.e. it is highly dependent upon degree of chlorination of the analyte. The detector response may vary as much as two to four orders of magnitude between monochloro- and polychlorinated biphenyls (Rote and Murphy 1971). A response factor is usually required for computation of the results (Webb and McCall 1973). Similar differences in response factors have been reported for chlorobenzenes (Lee et al. 1986; Ray and Jerome, Dept. of Fisheries and Oceans, St. Andrews, N.B., unpubl. data). Similarly, for analysis of dioxins using mass specific detection, the quantification is based on peak area measurements and comparison of these areas using isotopically labelled internal standards or calibration curves of external standards. It was observed that for thirteen well-defined tetra-CDF isomers, the response factors showed a threefold variation in the EI mode and up to twentyfold variation with the NCI mode (Rappe et al. 1983).

Since the 1970's, the PCB's in environmental samples have almost always been analyzed on packed columns and the results expressed in terms of technical formulation equivalents such as 1254 or 1260, etc. The sum of the heights of five to seven peaks in the chromatogram of the sample extract is compared with the sum of the heights of the same peaks of a standard solution of the chosen formulation. However, the results are normally biased since the peaks in the environmental samples never exactly match those of the standard solution for a variety of reasons like transformation, degradation, etc. Moreover, in the real world, the sample contamination rarely comes from a single formulation (Ray et al. 1984).

However, with the availability of capillary columns in the 1980's, the trend is to analyze the mixture in terms of individual components for more comprehensive information. It is expected that with the growing popularity of capillary columns, the use of packed columns will be slowly phased out or used only for reconnaissance survey and the use of capillary columns will become the standard norm for any in-depth study.

PCB's may also be quantified by perchlorination where all components are converted to dacachloro-biphenyl which, on GC, gives only one peak (Duinker et al. 1980; De Kok et al. 1982; Kerkhoff et al. 1982). The method is seldom used since it was reported that the conversion efficiencies varied from 60-100%, depending on the initial degree of chlorination (Duinker et al. 1980). The three techniques have been critically reviewed by Duinker et al. (1980).

The single most important factor contributing to our ability to identify specific trace organic substances in environmental samples has been the development of combined GC-MS. Negative ion chemical ionization mass spectrometry used as a detector for capillary GC is uniquely suited to measuring trace polyhalogenated organics in

environmental samples because of its high sensitivity for these compounds and its virtual transparency to other potentially interfering molecules (Kuehl et al. 1980). Furthermore, it provides molecular ion information, a very desirable feature, when examining complex environmental and biologial samples.

Interlaboratory comparisons for organochlorines in biota (Galloway et al. 1983) have pointed to the large variability in the analytical results from the participating laboratories. International Council for the Scientific Exploration of the Seas (ICES) has conducted several interlaboratory calibration studies on analyses of PCB's in biological tissues. The results of the last round robin test (Musial and Uthe 1983) indicated that the interlaboratory variance was too large to allow satisfactory interlaboratory comparisons. Obviously, the progress in our capability to accurately measure the OC's in the environment will largely depend upon the availability of certified reference materials in different phases of the aquatic environment (i.e. water, particulates, sediments and biota).

POLYCYCLIC AROMATIC HYDROCARBONS

The number of polycyclic aromatic hydrocarbons (PAH) that are most commonly determined in aquatic samples is only eight to ten. Among them are anthracene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(a)pyrene, benzo(e)pyrene, chrysene and perylene. Naphthalene and methylnapthalenes are also sometimes determined, although strictly, they do not belong to this category of compounds.

The analysis of PAH's in sediment, water or biota involves a three-step procedure:

1. solvent extraction
2. removal of interfering materials and separation into groups
3. determination of PAH in the extracts as total hydrocarbon or as individual components.

Solvent extraction

Several methods have been utilized for extraction of PAH's from aquatic organisms. These include simple steam distillation (Ackman and Noble 1973; Veith and Kiwus 1977), extraction with a variety of polar and nonpolar solvents (Farrington et al. 1976; Lawler et al. 1978) and alcoholic or aqueous base digestion followed by liquid-liquid partitioning (Farrington et al. 1976, 1985; Dunn and Fee 1979; Dunn 1980; Dunn and Armour 1980; Ramos and Prohaska 1981; Vassilaros et al. 1982; Lawrence and Das 1986). Some of these extraction procedures have been compared by Gritz and Shaw (1977) and Belisle et al. (1981).

Sediments are also similarly extracted by steam distillation (Veith and Kiwus 1977) and solvent extraction (Farrington and Tripp 1975; Lake et al. 1980). Alkali digestion in conjunction with solvent extraction has also been used to remove "tightly bound" hydrocarbons from the sediment and compared with results obtained by soxhlet extraction (Farrington and Tripp 1975). Wong and Williams (1980) compared three extraction methods for hydrocarbons in marine sediments and obtained comparable results with dried sediments but reported variable results on wet sediments. Lake et al. (1980) compared seven extraction procedures including soxhlet, reflux, alkali digestion and ball mill tumbler. The soxhlet extraction with 1:1 methanol-benzene and CH_2Cl_2 reflux were about equal in their extraction efficiency but the ball mill tumbler was only about 72% as efficient as the other methods.

Cleanup and fractionation

The organic extracts from the sediment and biota generally contain lipids and other non-hydrocarbon materials which must be separated from the hydrocarbons before they can be analyzed. In some cases, the hydrocarbons are separated into several fractions to facilitate analysis.

Cleanup and fractionation may be achieved by polarity, size or chemical separation techniques. In polarity separation, the hydrocarbons are separated from coextracted polar materials such as lipids by adsorption chromatography on silica gel (Ramos and Prohaska 1981; Lawrence and Das 1986), alumina (Vassaliros et al. 1982) or florisil (Dunn and Armour 1980; Lawrence and Das 1986; Lebo and Smith 1986).

In size separation, the large lipid molecules in the extract are separated from smaller hydrocarbon molecules. Sephadex LH20 has been used for cleanup as well as hydrocarbon polarity separation. The lipid fraction is eluted first, followed by the non-polar fraction and finally the aromatic portion (Giger and Schaffner 1978; MacLeod et al. 1982). A combination of LH20 and silica chromatography has also been used for cleanup and fractionation of sediment and biota extracts.

Sample extracts are often saponified prior to fractionation so that the polar lipid can be partitioned as their fatty acid salts and alcohols, leaving the hydrocarbons as clean extracts.

Removal of sulphur from sediment extract is also essential before GC or GC/MS and is accomplished by treating with either Cu (Blumer 1957) or mercury (Goerlitz and Law 1974).

Identification and quantitation

A variety of methods are available to determine the concentration and identify the individual components.

Gross quantification can be done by gravimetric measurement, infrared spectroscopy, ultraviolet spectroscopy or fluorescence spectroscopy (Zitko 1975). High resolution techniques available for identification and quantitation of the individual components are: liquid chromatography with ultraviolet fluorescence detector (Dunn and Armour 1980; Obana et al. 1981; Lawrence and Das 1986; Lebo and Smith 1986); gas chromatography with flame ionization detector (Ramos and Prohaska 1981; Vassaliros et al. 1982; Sporstøl et al. 1983) and GC-MS (Ramos and Prohaska 1981; Vassaliros et al. 1982; Lawrence and Das 1986).

As with chlorinated hydrocarbons, there are a variety of methods available for analysis of PAH's and the use is quite often determined by user bias and availability of instrumentation. Currently, HPLC is the recommended method for analysis of PAH (Fed. Register 1979). Laboratory intercomparison

studies have recently been reported for biological tissues (Farrington et al. 1985) and marine sediment samples (MacLeod et al. 1982).

CHLORINATED ETHERS

Halogenated diphenyl ethers (DPE) are comparable to PCB's, dibenzofurans and dibenzodioxins in their physicochemical properties. Both DPE's and PCB's have 10 congeners with 209 possible isomers each. DPE's may be found as impurities in technical pentachlorophenol and other chlorinated phenol formulations (Nilsson and Renberg 1974; Deinzer et al. 1978, 1979). It has also been used as a pesticide. Halogenated DPE's have been reported in fish and piscivorous birds (Andersson and Blomkvist 1981; Stafford 1983; Jaffe and Hites 1986).

Niimi (1986) analyzed the DPE's as follows: Fish samples were homogenized with Na_2SO_4 and extracted with dichloromethane. Lipid was removed by GPC and subsequently chromatographed on deactivated silica gel and eluted with 1% benzene:hexane. The eluate was further chromatographed on dry silica gel (130 for 3 h), eluted with hexane followed by benzene which contained the DPE components and analyzed by capillary EC-GC. Recoveries of the 16 DPE spiked samples ranged from 3% for decachloro-DPE to 97% for 2,2-,3,4,4-,6-DPE.

PRECISION, ACCURACY AND QUALITY ASSURANCE OF CHEMICAL DATA

Precision describes the degree to which the data are replicate and accuracy refers to correctness of data. "Unfortunately, there is no general agreement as to how accuracy is to be evaluated. Inaccuracy results from imprecision (random error) and bias (systematic error) in the measurement process" (ACS 1983). The accuracy of the results can be evaluated only when the true value is known or can be assumed.

"Quality assurance (QA) describes those techniques used to assess the quality of measurement process and the results." Furthermore, "the reliability and acceptability of environmental analytical measurements depend upon rigorous completion of all the requirements stipulated in a well defined protocol" (ACS 1983). Collaborative laboratory testing and the use of standard reference material must be prerequisites for analytical methods used for decision making processes. Analysis of standard reference material is an important component of the Quality Control program in any good analytical laboratory. This is the most effective approach to identify results that fluctuate beyond certain set limit (precision) or deviate significantly from true values (accuracy). In recent times, several new biological reference materials have been developed under various terminologies such as reference material (RM), certified reference material (CRM) and standard reference material (SRM).

Environmental Analytical Chemistry Subcommittee of American Chemical Society has developed detailed guidelines for data acquisition and data quality evaluation in environmental chemistry (ACS 1980, 1983). These guidelines should be followed if quality data are to be obtained in evaluating fisheries environmental problems, particularly for decision making for management and regulatory processes. However, unlike the vigorous quality assurance programs in the field, laboratory or instrumentation, there is no effective means to conduct such QA programs in the data acquisition and reduction system. The only assurance that the data acquisition and reduction is done correctly comes from the manufacturer and remains unchecked.

CONCLUSIONS

Problems encountered in analyses of trace organic contaminants in fishery environmental research have been reviewed. It is not intended to serve as a comprehensive listing of the relevant literature but rather an attempt to examine the problems encountered in specific instances. Deficiencies in various methods that are normally used for analysis of trace organic constituents in environmental samples have been pointed out and different ways of overcoming some of the problems have been discussed. The chemical methods consist of only three steps: solvent extraction; removal of interfering materials and preconcentration; and determination of the individual components of interest. But none of these steps are standardized, even for an ubiquitous contaminant like PCB. No single procedure is sufficient for the wide variety of applications in trace organic analysis. Quite often some of the methods are combined or modified to suit a particular application. However, all of the variations in the basic methods introduce their own characteristic problems and analytical errors. Even after 20 yr of experience in analysis of PCB's, the methods adopted for analysis vary widely and the attempts of interlaboratory comparison of the data have not yielded satisfactory results because of extremely large interlaboratory variance. The problem is more acute with pollutants that have gained environmental significance more recently.

There is much room for improvement in every step involved in analyses for trace organic contaminants. Moreover, there is a need for standard reference materials in different phases of the aquatic environment (i.e. water, particulates, sediment and biota) so that at least the individual laboratories may develop more confidence in their own work.

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